

$$u(v, T) ; h(p, T)$$

Review

Lost time:
$$\begin{cases} dh = v dp + dtq \\ du = dw + dtq = -p dv + dtq \end{cases}$$

$$du = c_v dT \quad \text{for ideal gas}$$

↑ internal heat capacity

$$dh = c_p dT \quad \text{for isobaric process}$$

and if you have a finite temperature change during a process

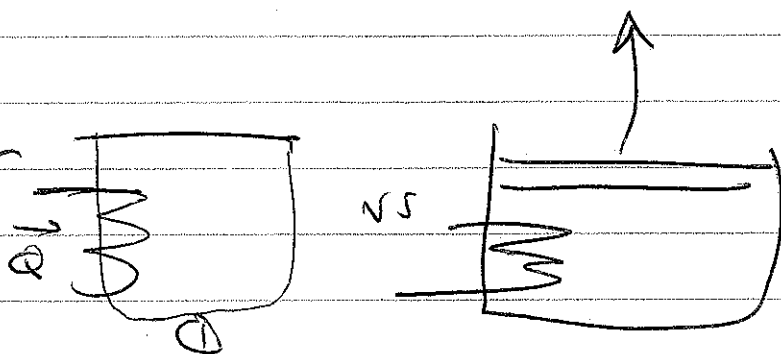
$$\Delta u = c_v \Delta T = \Delta Q \quad (\text{for isochoric heating}) \Rightarrow$$

$$\Rightarrow c_v = \frac{\Delta Q}{\Delta T} \quad T \text{ change associated with isochoric heating}$$

$$\Delta H = c_p \Delta T = \Delta Q \quad (\text{for isobaric heating})$$

$$c_p = \frac{\Delta Q}{\Delta T}$$

which are larger
 c_v or c_p ?



for same amount of ΔQ , all goes to T change in ①, but some to $p-v$ work in ②

application of 1st law to ideal gases

$$du = C_v dT$$

$$du = dw + dq$$

$$\left. \begin{array}{l} du = C_v dT \\ du = dw + dq \end{array} \right\} \Rightarrow \begin{array}{l} C_v dT = dw + dq \\ dw = -p dv \end{array}$$

assuming reversible expansion/compression

$$pV = RT$$

← comment on form $pV = \frac{m}{M} R T \Rightarrow$

$$\Rightarrow pV = RT$$

$$C_v dT = -\frac{RT}{v} + dq \Rightarrow$$

$$\boxed{C_v \frac{dT}{T} = -R \frac{dv}{v} + \frac{dq}{T}}$$

in the case of

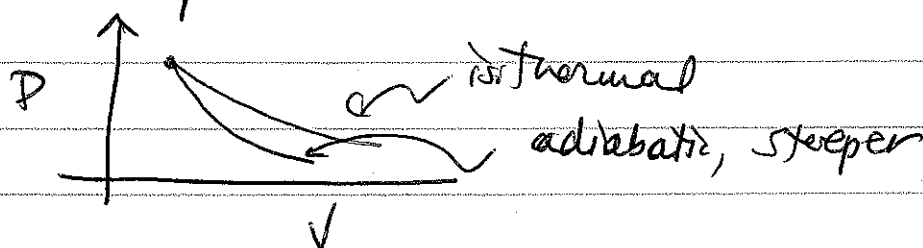
adiabatic expansion, $dq = 0$

$$C_v \frac{dT}{T} = -R \frac{dv}{v} \Rightarrow \int_{T_1}^{T_2} \frac{dT}{T} = -\frac{R}{C_v} \int_{v_1}^{v_2} \frac{dv}{v} \Rightarrow$$

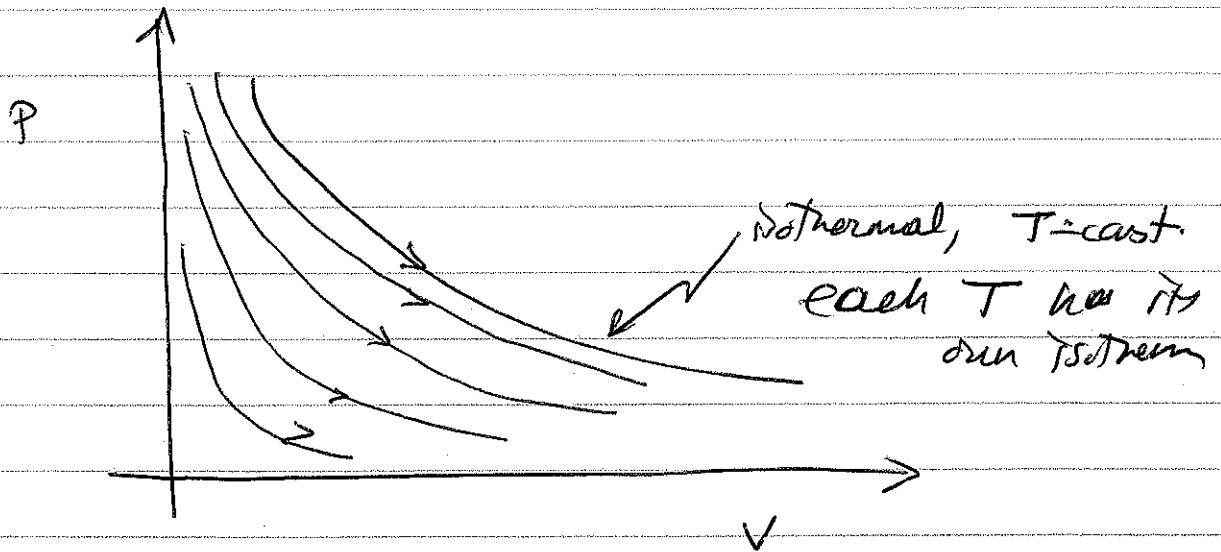
$$\Rightarrow \ln \frac{T_2}{T_1} = -\frac{R}{C_v} \ln \frac{v_2}{v_1} \Rightarrow$$

$$\boxed{\frac{T_2}{T_1} = \left(\frac{v_2}{v_1} \right)^{-R/C_v}}$$

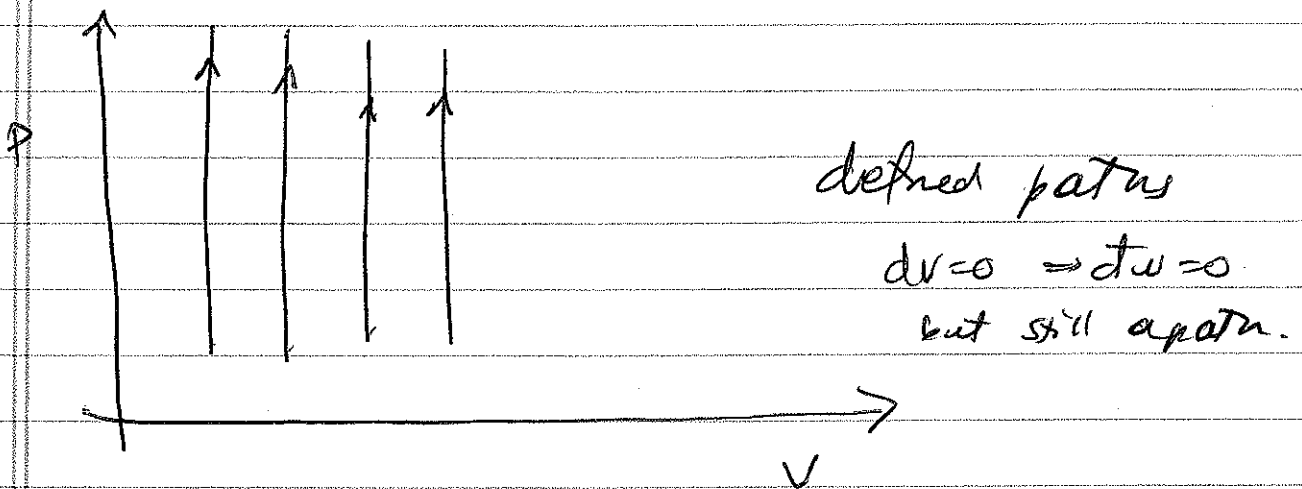
adiabatic expansion.



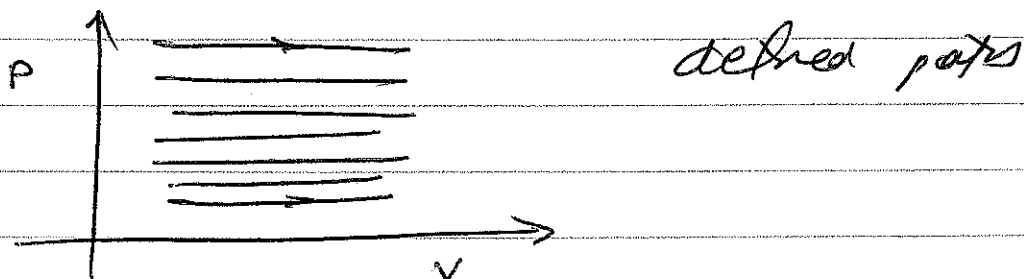
{ Defining "entropy" as a quantity that is useful for atmospheric processes

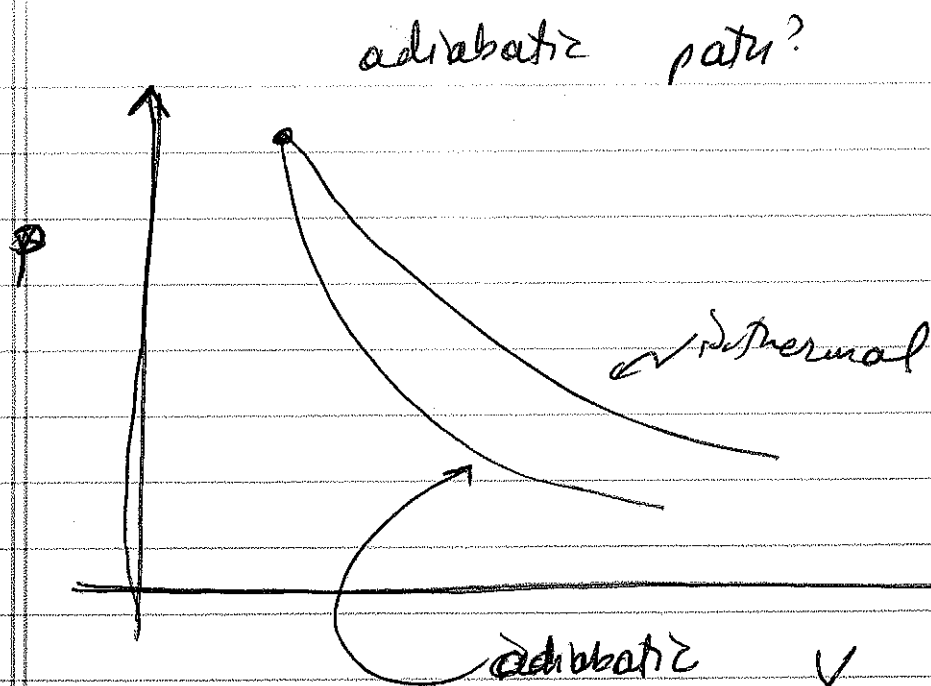


How about isobaric processes?



and isochoric





In adiabatic paths P, V, T change at the same time. But is something conserved?

Yes. Let's call that "thing" entropy S .

S will be a state function that is constant during a reversible adiabatic process

Definition of S .

→ Each reversible adiabat is unique, so it can be assigned a value of S .

→ Since S = const along a process where $\overbrace{Q_{rev}}^{\text{adiabat}} = 0$ then $dS \propto dq$

What is the problem that arises?
That S is a property, while Q is not. There

is a solution. In calculus, many inexact differentials can be made exact by finding an integrating factor. Perhaps there is one that:

$$dS = \frac{dQ_{\text{rev}}}{\lambda} \quad \lambda \text{ is integrating factor.}$$

Why choose this form? Well, we find the exact same analogy in reversible work. Recall:

$$dW_{\text{rev}} = -P dV \Rightarrow dV = -\frac{dW_{\text{rev}}}{P}$$

Even though dW_{rev} is not an exact differential dV is (Volume is a property) so P is an integrating factor. dW and dQ are similar

so we choose dS to have the same form as dV . Mathematically, there are infinite functions that can act as an integrating factor λ for dS . Since for dV we use V, P we select T for S (this makes sense, as P is a "driving" force for W , and T is a "driving force" for Q).

$$\text{So, } dS = \frac{dQ_{\text{rev}}}{T}$$

definition of entropy.

So " S " is what we call "entropy" and is
 defined as

$$ds = \frac{(dq)_{\text{rev}}}{T}$$

intensive (little s)

$$dS = \frac{(dQ)_{\text{rev}}}{T}$$

extensive (large S)

ds is to dq what dv is to dw .

$$dq = T ds$$

ds is the
 "driving force" for heat

$$dw = p dv$$

dv is the "driving force"
 for work.

changes in S cause heat flow.
 (or are a consequence of)

S has units of energy. Based on its temperature

definition, we can define S changes for two types of processes:

$$\begin{aligned} ds &= 0 \\ \Delta S &= 0 \end{aligned}$$

adiabatic
reversible process

$$ds = \frac{(dq)_{\text{rev}}}{T} \Rightarrow \Delta S = \frac{(\Delta Q)_{\text{rev}}}{T}$$

rev. isothermal process
@ temperature T

Note: if process not reversible, then $\frac{dq}{T}$ is not ds !

Entropy and max efficiency of engines

→ Some concepts

Heat engine: A device that converts heat (generated, e.g. by combustion) into mechanical (pv) work. It always operates on a cyclic process (because of spatial, heat, etc. limitations).

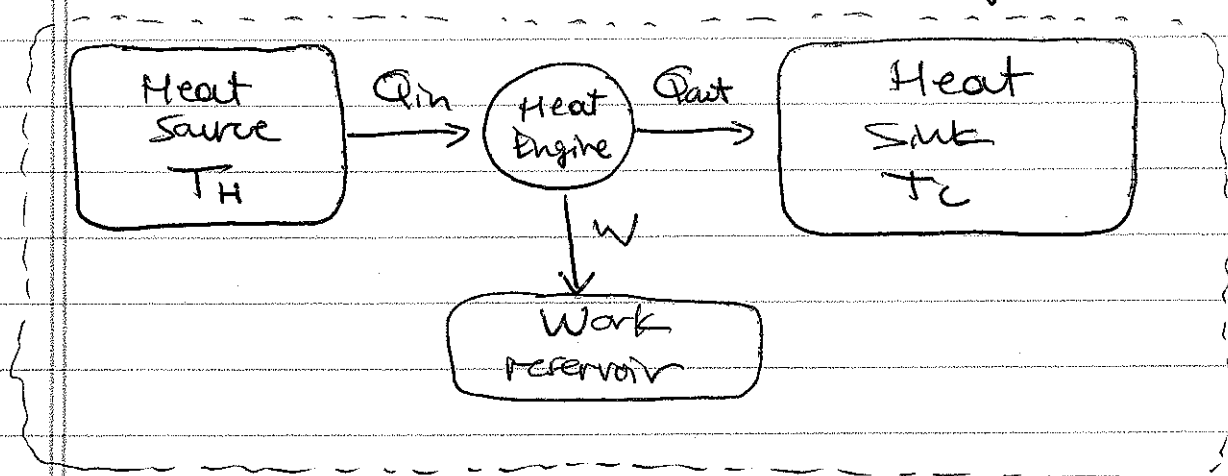
Efficiency of engine: $\mathcal{E} = \frac{W}{Q}$ \leftarrow work obtained per cycle
 \leftarrow heat supplied per cycle

for engineers, maximizing \mathcal{E} was the primary objective (and still is) of engine design.

→ Formulating the problem:

Take a heat engine (don't worry about technology, "how") and assume it operates reversibly (i.e., without energy losses from friction, and other irreversible processes)

and link it to a very large heat source of temperature T_H and a very large heat sink of temperature T_C . These are the source of heat, and recipient of excess (unused) heat in a cycle, respectively.



all this in a closed, insulated boundary.

Now take one cycle of the heat engine, and see what happens:

$$\Delta S_{\text{total}} = 0 = \Delta S_{\text{H, source}} + \Delta S_{\text{H, sink}} + \Delta S_{\text{H, by}} + \Delta S_{\text{w.r.}}$$

↑
source
↑
sink
↑
heat engine
↑
work
reservoir

cyclic process,
you end up where
you started from

$$\Delta S_{\text{univ}} = 0, \text{ because there is no heat exchange (adiabatic)}$$

$\Delta S_{H.Eng} = 0$, because the engine is brought to its original state

↙ b/c heat is "lost" from the H-source

$$\Delta S_{H-source} = - \frac{Q_{in}}{T_H}$$

$$\Delta S_{H-sink} = \frac{Q_{out}}{T_C}$$

large sink: we assume taking out same heat does not affect T

$$\text{So: } 0 = \Delta S_{H-source} + \Delta S_{H-sink} = - \frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_C} \Rightarrow$$

$$\Rightarrow \frac{Q_{out}}{T_C} = \frac{Q_{in}}{T_H} \quad (1)$$

Now, conservation of energy (1st law) applied to the engine gives $\Delta U = 0 = (Q_{in} - Q_{out}) - W \Rightarrow$
 $\Rightarrow W = Q_{in} - Q_{out} \quad (2)$

Substituting (1), (2) into the definition of \mathcal{E} gives:

$$\mathcal{E} = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_C}{T_H} \quad (3)$$

(3) is the maximum efficiency you can ever get with a heat engine. In case where you have irreversible processes, $W < W_{rev}$, so \mathcal{E} is reduced.

$\mathcal{E} < 1$, so you can never make a "perfect" engine that converts all heat to work. (That would need a infinitely hot source or a sink @ absolute zero).

Cars: heat engine $\nearrow T_{source} \sim 100^\circ\text{C} = 373$
 $\searrow T_{sink} \sim 20^\circ\text{C} = 293$

$$\mathcal{E} = 21\%$$

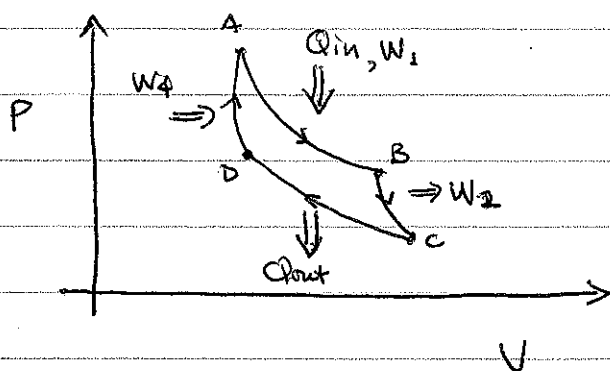
Power plants: $\left. \begin{array}{l} T_{source} \sim 250^\circ\text{C} \\ T_{sink} \sim 20^\circ\text{C} \end{array} \right\} \mathcal{E}_{max} = 44\%$

That is why internal combustion engines are such a bad idea (from a GW and full wage perspective), because you waste at least 80% of fuel.

Power plants are much more efficient

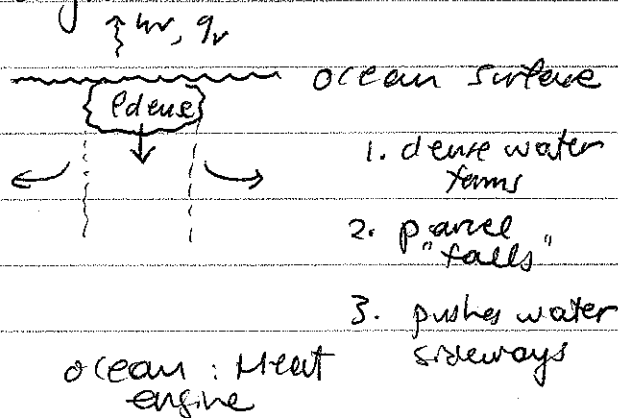
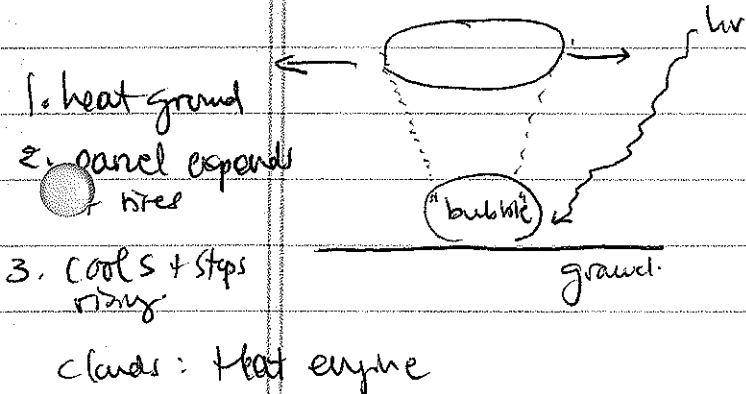
Other technologies (e.g. fuel cells) that do not operate on heat engine principles are much more efficient (theoretically, up to 80%).

Side note: The max \mathcal{E} is also equal to the efficiency of the Carnot cycle



- A \rightarrow B: Isothermal expansion Q_{in}, W_1
- B \rightarrow C: Adiabatic expansion W_2
- C \rightarrow D: Isothermal compression Q_{out}, W_3
- D \rightarrow A: Adiabatic compression W_4

Question: Do processes in the atmosphere & oceans exhibit a heat-engine configuration?

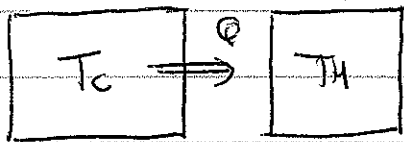


→ Pass around article about Carnot cycle analysis of hurricanes.

Second law of Thermodynamics

→ It says which processes that obey the first law are possible

eg. flow of heat from a cold object to a hot one.



Obeys the first law: $\Delta U = Q$
Does not occur spontaneously.
How can we quantitatively show this?

→ The total amount of entropy change for the process and its surroundings must be nonnegative for the process to be possible;

$$\Delta S_{\text{total}} \geq 0$$

Second law.

ΔS_{total} means the S of the system and its surroundings if they are connected

Isolated systems

Try it for the example of heat flowing from hot to cold object.

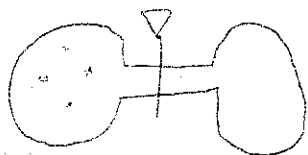
- In that sense, if a system is isolated, or, if the total energy is fixed, the system would tend towards the highest entropy state.
- Only for a cyclic reversible or a reversible adiabatic process does $\Delta S = 0$. However, all processes in nature are at least to some degree, irreversible (because changes are done fast and not in increments). Therefore in nature, ΔS_{total} always > 0 .

So, to assess whether a process can happen or not:

1. we calculate ΔS of the process and its surroundings
2. if $\Delta S_{\text{total}} > 0$, the process will happen and spontaneously.
3. if $\Delta S_{\text{total}} < 0$, the process will not happen.
4. if $\Delta S_{\text{total}} = 0$, then we have a reversible process and the system is in equilibrium at all times.

So what is entropy?

1. It is a measure of the "disorder" of a system. Example of notes:



vs.



The larger volume allows larger # of possible configurations → This also means the system is more "disordered" or "more spread out" at a given time.

molecules are located. Entropy is a ^{quantitative} way of determining whether a system becomes more disordered after a process. Since nature likes to decrease order (or increase randomness) This translates to nature always wanting to increase the entropy of a system.

In terms of the ^{useful} work you can get from a process, entropy is related to the amount of unavailable energy, or the amount of energy that cannot be converted to work.

Energy - entropy principles :

→ At constant energy (isolated system), the entropy becomes max.

→ At constant entropy (reversible ^{for adiabatic} system), the energy tends to a minimum.

Combined 1st and 2nd laws

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○ 1st law. $du = +dw + dq = -pdv + dq$ ①

2nd law $\int ds \geq 0 \sim ds = \frac{(dq)_{rev}}{T}$

Since u is a state function, we can always come up with a reversible path that has a $(dq)_{rev}$ associated with it, so that $(dq)_{rev} = (ds)T$ ②

Combining ① and ②, we get:

$$du = -pdv + Tds$$

• This is known as the "fundamental equation" of thermodynamics

• It is also known as "combined 1st + 2nd law"

The above is in internal energy form, intensive.

You can also have it in the enthalpic form:

$$dh = vdp + Tdq$$

②

$$dh = vdp + SdT$$

fundamental equation, enthalpic form.

• You can also have the extensive forms:

$$dU = -p dV + T dS$$

$$dH = V dp + S dT$$